A Solvent-Extraction Study of the Thermodynamics of *m*-Iodoaniline and the Proton Ionization of the *m*-Iodoanilinium Ion

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The distribution coefficients of *m*-iodoaniline between a petroleum ether fraction and aqueous sodium chloride solutions were determined at different temperatures. The activity coefficients of the amine in aqueous sodium chloride solutions, and the salting coefficients were determined at different temperatures. The results conformed with the Debye theory of salt effects. The proton ionization constant in terms of molalities (Km), the thermodynamic proton ionization constant of the aminium ion (K_O), the basic dissociation constant of the amine (Kb)m, the basic dissociation constant of the amine in pure water $(Kb)_O$, the standard free energy change ΔG^O, the standard enthalpy change ΔH^O, and the standard entropy change ΔS^O were evaluated for the proton ionization of the *m*-iodoanilinium ion.

Key words. Thermodynamics, Proton ionization, *m*-Iodoanilinium ion.

Introduction

During a study of the effect of electrolytes on the rate of diazotization of *m*-iodoaniline, it was found (Aboul-Seoud *etal* 1981) the proton ionization constant of the *m*-iodoanilinium ion was determined in presence of sodium chloride solutions of different ionic strengths. Certain thermodynamic parameters such as the activity coefficient of *m*-iodoaniline in aqueous sodium chloride solutions, and the basic dissociation constant of the amine, at different temperatures were evaluated. The values were to be combined (Aboul-Seoud *etal* 1981) with the results of equilibrium (Schmid and Maschka 1941; Schmid and Ableidinger 1954) and kinetic measurements involving *m*-iodoaniline.

Those values were determined in this study by a modified distribution method (Farmer and Warth 1904; Williams and Soper 1930; Aboul-Seoud and Salama 1993) in which attention was directed to the choice of the extracting solvent, and of the analytical method.

The proton ionization constant of the *m*-iodoanilinium ion was determined by a number of investigators (Vandenbelt *et al* 1954; Biggs and Robinson 1961; Biggs 1961), however some of the results (Vandenbelt *et al* 1954) were described (Perrin 1965) as uncertain, and others (Biggs and Robinson 1961; Biggs 1961) as approximate.

Besides, nobody studied the effect of high ionic strengths on this constant.

Experimental

The distribution method (Farmer and Warth 1904) modified in several directions (Williams and Soper 1930; Aboul-Seoud

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and El-Hares 1964; Aboul-Seoud and Doheim 1966; Aboul-Seoud and El-Sherif 1971; Aboul- Seoud and Salama 1993) was used in this study.

A petroleum ether fraction (B.P90-130°C) was used as extracting solvent. This is not too volatile and does not react with any of the substances involved in this study. Unlike benzene, it is very slightly soluble in water (less than 5 mg/100 ml water at 20°C), so that there is no need for solubility corrections (Williams and Soper 1930) also, it does not lead to distribution coefficients which are inconveniently high (Farmer and Warth 1904; Williams and Soper 1930).

The *m*-iodoaniline in the organic phase was determined by ultraviolet spectrophotometry. Absorption curves for solutions of *m*-iodoaniline in petroleum ether, of different concentrations, showed that 295 mu was the wavelength of maximum absorption. Consequently, all spectrophotometric measurements of the concentration of *m*-iodoaniline in petroleum ether were carried out at this wavelength.

m-Iodoaniline was prepared (Wikander 1907) through diazotisation of the corresponding nitroaniline, followed by iodination (Vogel 1956) with potassium iodide, followed by reduction (West 1925) of the iodonitrobenzene to iodoaniline.

The amine was further purified by twice vacuum distillation, discarding the first portion of the distillate and the residue. m.p. 25°C.

An A. R. Sodium Chloride was used in this study. Petroleum ether fraction (B.P 90-130°C) was purified by shaking with concentrated sulphuric acid, water, sodium hydroxides solutions, water, followed by distillation.

m-Iodoanilinium chloride: Stock solution was prepared by dissolving the calculated amounts of amine and constant

boiling point hydrochloric acid in distilled water, and making up to the mark in a measuring flask.

Distribution coefficient measurements. 25 ml of petroleum ether, containing the calculated amount of amine, were equilibrated, at the desired temperature, with the suitable volume of boiled out distilled water, containing the calculated amount of sodium chloride. The two phases were then separated, and the amine was determined in the organic phase.

For accuracy in determining distribution coefficients, the volume of the aqueous phase was so arranged as to keep the amount of amine in that phase approximately equal to that in the organic phase, in which it was estimated, since the former was found by difference.

Also, the amine concentration was so arranged as to give an equilibrium concentration of amine, in the organic phase, nearly equal to that obtained in proton ionization constant measurements, in order to minimize any error due to association, hydration or other disturbing factors (Williams and Soper 1930).

Proton ionization constant measurements. These measurements were carried out by equilibrating a certain volume of petroleum ether with a certain volume of aqueous sodium chloride solution containing the calculated amount of *m*-iodoanilinium chloride.

The containers containing the above-mentioned solution were placed in a water bath, at the desired temperature. The containers were shaken from time to time. After one hour, a

Table 1

The distribution of *m*-iodoaniline between petroleum ether and aqueous sodium chloride solutions

Temp°C ± 0.05	NaCl mol dm^{-3}	NaCl molality	C_p/C_a $\pm 0.1\%$	m_p/m_a $\pm 0.1\%$	f_B $\pm 0.2\%$	k_m $\pm 0.2\%$
	0.00	0.000	8.75	11.89	1.00	
	0.25	0.251	9.23	12.49	1.05	
	0.50	0.504	10.50	14.14	1.19	
10						0.15
	1.00	1.018	12.92	17.25	1.45	
	2.00	2.080	18.29	23.89	2.01	
	3.00	3.192	26.88	34.31	2.89	
	0.00	0.000	9.74	13.23	1.00	
	0.25	0.251	10.27	13.89	1.05	
	0.50	0.504	11.68	15.74	1.19	
20						0.15
	1.00	1.018	14.38	19.19	1.45	
	2.00	2.080	20.36	26.61	2.01	
	3.00	3.192	30.00	38.30	2.90	
	0.00	0.000	10.83	14.72	1.00	
	0.25	0.251	11.43	15.46	1.05	
	0.50	0.504	13.00	17.51	1.19	
30						0.15
	1.00	1.018	16.00	21.36	1.45	
	2.00	2.080	22.70	29.67	2.02	
	3.00	3.192	33.57	42.87	2.91	
	0.00	0.000	12.06	16.39	1.00	
	0.25	0.251	12.73	17.22	1.05	
	0.50	0.504	14.47	19.49	1.19	
40						0.15
	1.00	1.018	17.82	23.78	1.45	
	2.00	2.080	25.38	33.16	2.02	
	3.00	3.193	37.69	18.13	2.94	

time which was found sufficient for the system to attain equilibrium, the petroleum ether phase was separated from the aqueous phase, and the amine was determined in the former phase by means of ultraviolet spectrophotometry.

These measurements were made at 10, 20, 30 and 40°C. All measurements were carried out in duplicate.
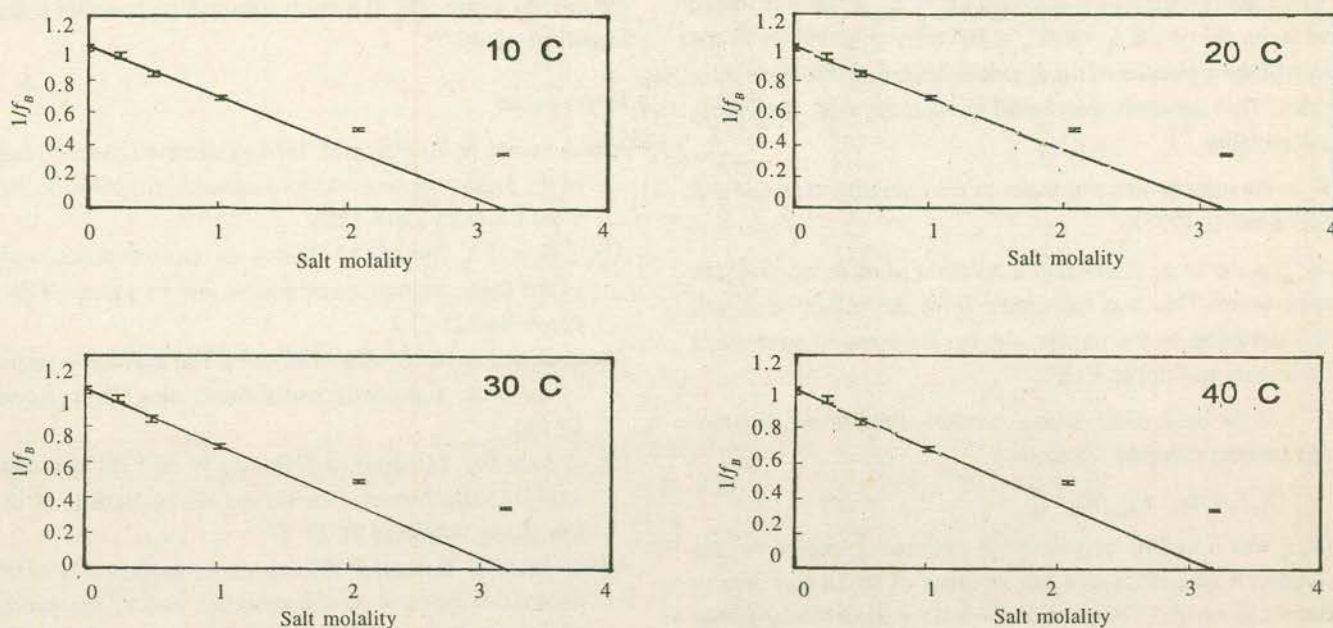
Results and Discussions

Thermodynamics of m-iodoaniline. Distribution studies, covering the range of amine concentration investigated, showed that the distribution of *m*-iodoaniline between petroleum ether and water was independent of the total amine concentration which, indicated that no association or compound formation took place in either phase (Treybal

1951). This was concluded from the linearity of the plot of the concentration of amine in the organic phase (Cp) versus its concentration in the aqueous phase (Ca), in distribution experiments carried out at 10, 20, 30 and 40°C.

In Table 1, Cp/Ca and mp/ma are the distribution coefficients in terms of molarities and molalities, respectively, of *m*-iodoaniline between petroleum ether and aqueous sodium chloride solutions (Aboul-Seoud and Salama 1993). The distribution coefficient was found to increase with salt molality and with temperature. f_B is the activity coefficient of the amine in the aqueous phase (Aboul-Seoud and Salama 1993). The plot of $1/f_B$ against $mNaCl$ was found to be linear upto a molality of one. This indicated that the results conformed in a general way and up to this molality to the

Table 2
The effect of temperature and salt concentration on the proton ionization of the *m*-iodoanilinium ion.

Temp°C ±0.05	NaCl mol dm⁻³	K_m 10⁴ ±0.3%	K_o 10⁴ ±0.3%	f_{H+}/f_{BH+}	K_w. 10¹⁴	$(K_b)_o$. 10¹² ±0.3%	$(K_b)_m$ 10¹² ±0.3%
	0.00	1.8		1.00			21.23
	0.25	1.39		1.23			29.57
	0.50	1.22		1.24			32.53
10			1.80		0.29	16.27	
	1.00	0.91		1.36			29.79
	2.00	0.41		2.16			22.22
	3.00	0.19		3.26			15.64
	0.00	2.51		1.00			35.65
	2.25	1.87		1.28			49.44
	0.50	1.26		1.67			52.51
20			2.51		0.68	27.09	
	1.00	1.29		1.34			50.55
	2.00	0.57		2.18			37.74
	3.00	0.27		3.19			26.51
	0.00	3.57		1.00			54.63
	0.25	2.53		1.34			75.44
	0.50	2.25		1.34			80.45
30			3.57		1.47	41.19	
	1.00	1.65		1.49			77.43
	2.00	0.72		2.47			58.01
	3.00	0.32		3.83			41.95
	0.00	5.08		1.00			76.52
	0.25	3.38		1.43			107.33
	0.50	3.11		1.37			114.17
40			5.08		2.91	57.31	
	1.00	2.30		1.52			110.64
	2.00	0.88		2.87			84.53
	3.00	0.43		4.03			58.60

Fig 1. $1/f_B$ vs. Salt molality.

Debye theory of salt effects (Debye 1927; Harned and Owen 1950a) k_m is the salting coefficient (Harned and Owen 1950b). This was obtained by plotting $\log f_B$ vs the sum of the molalities of the amine and sodium chloride, in the aqueous phase.
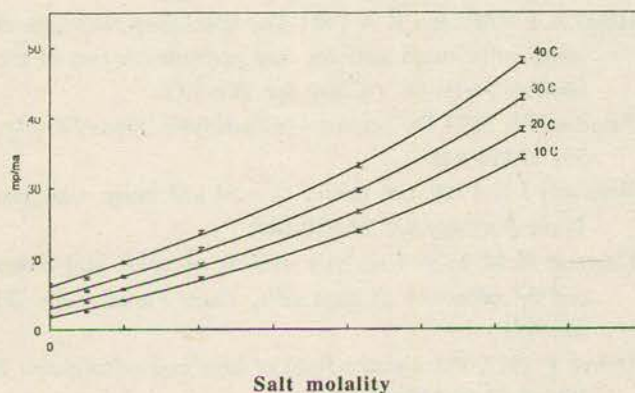

Salt molality

Fig 2. mp/ma vs. Salt molality.

Table 3

The thermodynamic parameters for the proton ionization of the *m*-iodoanilinium ion

Temp °C	$\Delta G°$ Kcal mol⁻¹	$\Delta H°$ Kcal mol⁻¹	$\Delta S°$ e. u
10	4.85±0.02		-0.20±0.01
20	4.83±0.02		-0.11±0.01
		4.80±0.02	
30	4.78±0.02		0.05±0.01
40	4.72±0.02		0.25±0.01

The linearity of this plot was in concordance with the Setchenow relationship (Harned and Owen 1950b), and with the findings of Randall and Failey (1927 a,b&c).

Thermodynamics of the proton ionization of the m-iodoanilinium ion. The concentration of the *m*-iodoanilinium chloride solution was 1.5×10^{-4} mol dm⁻³.

In Table II the values of the *mp/ma* ratio, used in calculating the proton ionization constants, were obtained from the plots of *mp/ma* vs salt molality and corresponded to molalities equal to the sum of those of the sodium and *m*-iodoanilinium chlorides. Account was thus made of the effect of the presence of the aminium ions, on the distribution coefficients (Williams and soper 1930). K_m is the proton ionization constant, in terms of molalities, of the *m*-iodoanilinium ion,

$$K_m = m_{B'} \, m_{H+}/m_{BH'}$$

K_o is the thermodyanmic proton ionization constant of the *m*-iodoanilinium ion,

$$K_o = (f_{B'} \, f_H + / f_{BH+}) \, (m_B \, m_{H+}/m_{BH+}) = (f_B \, f_{H+}/f_{BH+}) \, Km,$$

Where f_B and f_{BH+} are the activity coefficients and m_B and m_{BH+} are the molalities, of the amine, and of the aminium ion, re, in the aqueous phase.

K_o was obtained from the relation between K_m and the sum of the molalities of the sodium and *m*-iodoanilinium chlorides, obtained with the aid of a regression program. K_o is the value at zero molality.

K_m was found to decrease with salt molality.

The activity coefficient quotient (f_{H+} / f_{BH+}) was calculated with the aid of the f_B values, at the respective values of the sum of the molalities of the *m*-iodoanilinium, and sodium chlorides. This quotient was found to increase with increasing salt molality.

K_w is the ionic product of water at zero molality (Harned and Mannweiler 1935).

$(K_b)_o$ is the basic dissociation constant of *m*-iodoaniline, in pure water. This was calculated from the values of K_w and K_o, assigning to the former a value referring to pure water (Williams and Soper 1930).

$(K_b)_m$ is the basic dissociation constant of the amine, in aqueous sodium chloride solutions,

$$(K_b)_m = m_{H+} \cdot m_{OH}/K_o.$$

$(K_b)_m$ was found to increase with salt concentration, to pass through a maximum at a salt molality of 0.625 and then to decrease again. This concords with earlier conclusions (Bronsted 1927 and 1928). The initial increase in the values of $(K_b)_m$ may be compared with earlier findings Bronsted 1927 and 1928; Dawson 1928) according to which the presence of moderate salt concentrations caused an increase in the values of K_b, which might amount to as much as 40% in the presence of 0.02 M salt (Harned and akerlof 1928).

K_o was found to be linearly related to temperature according to the relation $pK_o = (1048.55/T) + 0.0014$.

Thermodynamic parameters. For the proton ionization of the *m*-iodoanilinium ion, the standard free energy change ($\Delta G°$), the standard enthalpy change ($\Delta H°$), and the standard entropy change ($\Delta S°$) were calculated (Table 3). The fact that $\Delta H°$ was independent of temperature, in the range 10-40°C, indicated that, in that temperature range, the difference of the partial molar heat capacity, in the proton ionization of the *m*-iodoanilinium ion, (ΔH_p) equalled zero.

The substituent constant (I) (Fujita *et al* 1964) was found to be 1.05 for the *m*-iodo group the Hammett substitution constant (σ) (Hammett 1940) was 0.40.

Conclusions

K_m was found to decrease with salt molality. The activity coefficient quotient increased with increasing salt molality. The basic dissociation constant of the amine in aqueous sodium chloride solutions increased with salt concentration, to pass through a maximum at a salt molality of 0.625, and then decreased again. This concords with the conclusions already drawn by Arrhenius and Bronsted. K_o was found to be related to temperature according to the relation $pK_o = (1048.55/T) + 0.0014$. The substituent constant I was found to be 1.05 for

the *m*-iodo group. The Hammett substitution constant σ was found to be 0.40.

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